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(54) **Production of chlorine dioxide in an electrolytic cell.**

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**EP-A- 0 266 127**  
**EP-A- 0 293 151**  
**FR-A- 2 504 559**

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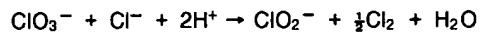
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**Description**

The present invention relates to the production of chlorine dioxide in substantially pure form, i.e. substantially free from chlorine.

Chlorine dioxide is widely used as a bleaching chemical and is known to be produced by reduction of sodium chlorate in an acid aqueous reaction medium. The reaction whereby chlorine dioxide is formed, is represented by the equation:



Generally, therefore, chlorine is co-produced with the chlorine dioxide.

Processes are known wherein the chlorine so-produced is reduced chemically, for example, using sulphur dioxide or methanol, thereby producing chloride ions for the process *in situ*. Such processes employ sulphuric acid as the acid source, resulting in sodium sulphate by-product.

In addition, there have been suggestions in the art to use electrolytic procedures for the production of chlorine dioxide. In this regard, the applicants are aware of U.S. Patents Nos. 3,904,495, 3,904,496, 3,920,801, 4,308,117, 4,324,635 and 4,456,510.

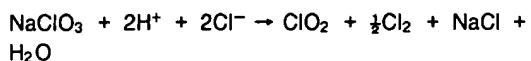
With the exception of the latter patent, in each instance, chlorine dioxide is produced in conjunction with chlorine from aqueous chlorate solution in the anode compartment of a multicompartiment cell. In U.S. Patent No. 4,456,510, an aqueous sodium chlorite solution is electrolyzed to produce chlorine dioxide.

One process described in the prior art for the electrolytic production of chlorine dioxide is contained in EP-A-0293151 (equivalent to U.S. Patent No. 4,731,169), wherein chlorate ions are reduced by electrolytically-produced chlorite ions at an acid normality of at least 7 normal sulfuric acid, the chlorite ions being produced by electrochemical reduction of a portion of the chlorine dioxide produced by the process. EP-A-0293151 claims a priority date of 29 May 1987 but was not published until 30 November 1988.

In accordance with the present invention, there is provided an electrolytic process for the production of chlorine dioxide which is carried out in the cathode compartment of a cation-exchange membrane divided cell in which co-produced chlorine is reduced electrolytically in the cathode compartment in which is positioned a high surface area cathode having a three-dimensional electroconductive surface. Chlorate ions, usually in the form of an aqueous sodium chlorate solution, are fed to the cathode compartment in which are provided hydrogen ions and chloride ions. The chlorate ions are reduced with the hydrogen ions and chloride

ions in the cathode compartment to produce the chlorine dioxide, which is vented from the cathode compartment, while an electric current is applied to reduce the co-produced chlorine to chloride ions. Hydrogen ions are electrolytically formed in the anode compartment and are transferred from the anode compartment to the cathode compartment. In this way, high purity chlorine dioxide is produced electrolytically from chlorate feed.

The chlorine dioxide is generated chemically in the cathode compartment according to the equation:



The chlorine co-produced with the chlorine dioxide in the cathode compartment in accordance with this equation is electrolytically reduced to chloride ions, leaving the product chlorine dioxide exiting from the cathode compartment substantially free from the chlorine.

Water is fed to the anolyte compartment of the cell, after an initial charge of an oxy-acid. The electrolysis carried out in the cell produces oxygen gas, which is vented from the anode compartment, and hydrogen ions, which migrate across the cation-exchange membrane into the anode compartment to provide hydrogen ions therein for the chemical reaction producing chlorine dioxide therein. For each gram-atom of chlorine reduced electrochemically in the cathode compartment to  $\text{Cl}^-$ , one mole of  $\text{H}^+$  is transferred into the cathode compartment, thereby providing 1 mole of the two moles of hydrogen ions and chloride ions required for continuous operation of the chlorine dioxide-producing reaction. Accordingly, the cathode compartment requires the feed of 1 mole of sodium chlorate, 1 mole of hydrogen ions and 1 mole of chloride ions to maintain the chlorine dioxide production as a continuous process.

Alternately,  $\frac{1}{2}$  mole of chlorine may be fed to the cathode compartment along with one mole of sodium chlorate. In this case, two moles of  $\text{H}^+$  are transferred from the anode compartment to the cathode compartment to satisfy the hydrogen ion requirement of the process, while the  $\frac{1}{2}$  mole of chlorine fed to the cathode compartment and the  $\frac{1}{2}$  mole of chlorine co-produced in the cathode compartment are electrochemically reduced to provide the two moles of chloride ions.

The invention is described further, by way of illustration, with reference to the accompanying drawings, wherein:

Figure 1 is a schematic representation of an electrolytic cell for the production of chlorine dioxide in accordance with one embodiment of the invention;

Figure 2 is a schematic representation of the integration of an electrolytic cell for the production of chlorine dioxide with an electrolytic cell for the production of sodium chlorite, in accordance with another embodiment of the invention; and

Figure 3 is a schematic representation of the integration of an electrolytic cell for the production of chlorine dioxide with an electrolytic cell for the production of sodium hydroxide and chlorine.

Referring first to Figure 1, there is shown therein an electrolytic cell 10 for the production of chlorine dioxide in accordance with one embodiment of the invention. Aqueous sodium chlorate solution is fed by line 12 to the cathode compartment 14 of the cell 10, which contains a three-dimensional electrode. An acid, preferably hydrochloric acid, also is fed to the cathode compartment 14 by line 16.

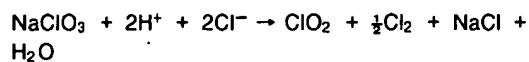
The aqueous sodium chlorate solution fed by line 12 has a concentration sufficient to establish, at its flow rate, a relatively high concentration of sodium chlorate in the cathode compartment 14, generally greater than about 5 molar, preferably about 5 to about 6.5 molar. Usually, the sodium chlorate feed solution has a concentration in the range of about 3 to about 7 molar.

The cell 10 has a cation-exchange membrane 18 separating the cathode compartment 14 from an anode compartment 20. After an initial charge of an oxy-acid, usually sulfuric acid, water is fed by line 22 to the anode compartment 20 and hydrogen ions produced by electrolysis of the anolyte migrate across the cation-exchange membrane 18 to the cathode compartment 14. The anolyte sulfuric acid solution is recirculated by line 23.

The hydrogen ion migration across the cation-exchange membrane 18 and the feed of hydrochloric acid by line 16 establish a total acid normality in the cathode compartment 18 of at least about 0.01 normal, preferably at least about 0.05 normal.

The oxygen co-produced in the electrolysis step in the anode compartment is vented by line 24 from the anode compartment 20.

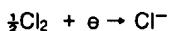
In the cathode compartment 14, the sodium chlorate fed by line 12 reacts chemically with the hydrogen ions and chloride ions fed by line 16, the electrolytically-produced hydrogen ions transferred across the cation-exchange membrane and the chloride ions electrolytically produced in the cathode compartment 14 as described below, to form chlorine dioxide and chlorine in accordance with the equation:



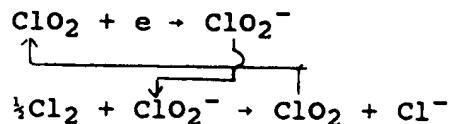
5 One half of the hydrogen ion requirement is provided by the acid fed by line 16 with the remainder of the hydrogen ion requirement is provided by the hydrogen ions transferred from the anode compartment 20.

10 The co-produced chlorine is reduced under the electrochemical conditions which exist in the cathode compartment 14, selectively with respect to the chlorine dioxide present therein. The chloride ions so produced provide half the chloride ions for the chemical reduction of the chlorate, with the remainder of the chloride ions being provided by the hydrochloric acid feed in line 16, or from some other convenient external source of chloride ions, such as sodium chloride.

15 Depending on the electrolytic conditions in the cathode compartment, the chloride ions may be produced directly from the co-produced chlorine by electrochemical reduction, in accordance with the equation:



20 or indirectly by reduction chemically with chlorite ion electrolytically produced from chlorine dioxide, in accordance with the equations:



25 In this latter procedure, the chlorite ion formation is controlled so as to avoid further electrolytic reduction of chlorite, which inefficiently produces chlorine.

30 The chlorine concentration in the product off-gas stream in line 26 may be monitored and the current applied to the cell is used to control the chlorine concentration.

35 The feeds of sodium chlorate by line 12 and of chloride ions by line 16 as well as the electrochemically-produced chloride ions establish a chlorate to chloride ion ratio in the cathode compartment 14 generally at least about 1:1, preferably about 2:1 to about 4:1.

40 The electrode potential which is applied to the cathode is more positive than -1 volt as compared with a saturated calomel electrode (SCE) and as determined at the current feeder to the cathode and more negative than the open circuit potential under the prevailing conditions, preferably about -0.2 volt.

45 The electrode potential of the cathode refers to the solution potential measured at the current feeder, in analogous manner to a flat plate electrode. A three-dimensional electrode, such as employed

herein, inherently has a distribution of potential within the structure and the actual potential will depend on the location of determination and may be more negative than -1 volt vs. SCE.

The cathode compartment 14 preferably is maintained at an elevated temperature to assist in the rate of chlorine dioxide formation. Usually, a temperature in excess of about 50°C is employed, preferably about 60° to about 70°C.

Alternatively, chlorine can be fed to the cathode compartment 14 in place of the hydrogen ions and chloride ions in line 16, for selective reduction to chloride ions along with the selective reduction of the co-produced chlorine. In this case, the anolyte feed is increased so as to provide twice as much hydrogen ion migration across the membrane 18 and hence provide all the hydrogen ion requirement of the cathode compartment 14.

The chlorine dioxide produced in the chemical reaction, substantially free from chlorine, is vented from the cathode compartment 14 as the product gas stream by line 26. This chlorine dioxide stream may be utilized further, as described, for example, with respect to the embodiment of Figure 2 below.

The by-product sodium chloride from the chemical production of chlorine dioxide is removed from the cathode compartment as an aqueous solution by line 28. This aqueous sodium chloride solution may be forwarded to a chlorate cell for electrolytic conversion to aqueous sodium chlorate solution for recycle to the cathode compartment 14 to provide at least part of the sodium chlorate in line 12.

The cathode employed in the cathode compartment 14 is a high surface area electrode having a three-dimensional electrolyte-contacting surface, which permits a long contact time between the reactants.

The term "high surface area" in relation to the cathode refers to an electrode of the type wherein the electrolyte is exposed to a large surface area of electrode surface in comparison to the physical dimensions of the electrode. The electrode is formed with interstices through which the electrolyte flows, and so has a three-dimensional surface of contact with the electrolyte.

The high surface area cathode may be the so-called "flow through" type, wherein the electrode is formed of electroconductive porous material, for example, layers of electroconductive cloth and the electrolyte flows through the porous structure generally parallel to the current flow while being subjected to electrolysis, and thereby is exposed to the high surface area of the mesh of the electrode.

The high surface area cathode also may be the so-called "flow by" type, wherein the electrode comprises a packed bed of individual electroconductive particles and the electrolyte flows through

the packed bed generally perpendicular to the current flow while being subjected to electrolysis, and thereby is exposed to the high surface area of the electroconductive particles in the packed bed.

5 The electrode may be constructed of materials having a low overpotential or preferably high overpotential, particularly graphite, for the reaction  $\text{Cl}_2 \rightarrow \text{Cl}^-$ . As is well known to those skilled in the electrochemical art, the overpotential of an electrode towards the electrochemical reaction  $\text{Cl}_2/\text{Cl}^-$  refers to the relationship of the potential applied to the electrode to the equilibrium potential to sustain the electrochemical reaction at a reasonable rate. If the electrode potential is close to the equilibrium potential, then the electrode is considered to have a "low" overpotential while, if a much more negative potential is required to achieve a significant reduction rate, then the electrode is considered to have a "high" overpotential.

20 Materials of construction of such low overpotential electrodes are known and are employed in the so-called "Dimensionally Stable Electrodes". Such electrodes generally comprise a substrate, which is titanium, zirconium, tantalum or hafnium, having an electroconductive coating thereon, which may be a precious metal, for example, platinum; a precious metal alloy, for example, a platinum-iridium alloy; a metal oxide, for example, ruthenium oxide or titanium dioxide; a palatinate, for example, lithium palatinate or calcium palatinate; or mixtures of two or more of such materials. Any of these materials may be employed to provide the material of construction of a low overpotential cathode.

25 The cell 10 in which the electrolytic production of chlorine dioxide is effected in accordance with the present invention may have any convenient construction. Usually, the cell is divided into anolyte and catholyte compartments 20 and 14 by an ion-exchange membrane 18, usually a cation-exchange membrane so as to promote hydrogen ion transfer and to prevent the interaction of gases produced at the anode, usually oxygen, with the chlorine dioxide and the electroreduction at the cathode. The anode of the cell may be constructed of any desired electroconductive material, for example, graphite or metal.

30 Referring now to Figure 2, there is shown the integration of the chlorine dioxide generator 10 of Figure 1 with a chlorate cell 30 and a chlorite-generating cell 32, as described in more detail below. In this embodiment, the sodium chloride by-product in line 28 is forwarded to the chlorate cell 30, wherein the sodium chloride is electrolyzed to form sodium chlorate, which is recycled by line 12 to the chlorine dioxide generator 10. By-product hydrogen from the electrolysis in the chlorate cell 30 is vented by line 34.

Chlorine dioxide formed in the generator 10 is forwarded by line 26 to the cathode compartment 36 of the chlorite-generating cell 32. Sodium chloride is fed by line 38 to an anode compartment 40 of the chlorite-generating cell 32. Anodic electrolysis produces chlorine while sodium ions migrate across a cation-exchange membrane 42 separating the anode compartment 40 from the cathode compartment 36. In the cathode compartment, the chlorine dioxide forwarded by line 26 forms chlorite ions, resulting in a discharge of sodium chlorite solution in line 44 from the cathode compartment 36.

Depleted sodium chloride solution exiting the anode compartment 40 is recycled by line 46. The chlorine formed in the anode compartment 40 is passed by line 48 to the cathode compartment 14 of the chlorine dioxide generator 10. In comparison to Figure 1, all the hydrogen ions and chloride ions for the cathodic production of chlorine dioxide are produced *in situ* in compartment 14 from the chlorine fed by line 48 and hydrogen ion migration. This result is achieved by increasing the current supplied to the cell from 1 Faraday to 2 Faradays per mole of chlorine dioxide produced.

The overall process between the chlorine dioxide generator 10 and the chlorite cell 32 (theoretically) requires no additional input of hydrogen ions and/or chloride ions, since all the hydrogen ions and/or chloride ions required by the chlorine dioxide generator are provided within the system and no chlorine output requires to be handled. Further integration with the chlorite cell produces a system wherein the only inputs are sodium chloride and power and the only outputs are sodium chlorite, hydrogen and oxygen.

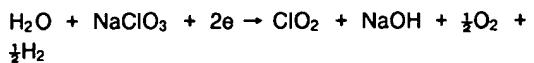
A modification of the procedure of Figure 2 involves forwarding sodium chloride from the anolyte chamber 40 of the chlorite-generating cell 32 to the chlorite cell 30. In addition, any hypochlorous acid in the hydrogen off-gas stream 34 may be condensed and recycled to cathode compartment of the chlorine dioxide generator 10.

In Figure 3, there is illustrated integration of the chlorine dioxide generator 10 with a caustic-chlorine cell 50. In this case, the sodium chloride by-product, along with unreacted sodium chlorite, is forwarded by line 28 to the anode compartment 52 of the caustic-chlorine cell 50. An electrolyte is forwarded by line 54 to the cathode compartment 56 of the caustic-chlorine cell 50, separated from the anode compartment 52 by a cation-exchange membrane 58.

Chlorine produced in the anode compartment 52 is forwarded as an aqueous solution in the unreacted sodium chlorite, by line 60 to the cathode compartment of the chlorine dioxide generator 10. Sodium hydroxide is recovered from the cath-

ode compartment 50 as product in line 62 and by-product hydrogen gas is vented by line 64.

The overall process for the Figure 3 embodiment is depicted by the equation:



10 The input requirements are sodium chlorite and power to produce chlorine dioxide, sodium hydroxide, oxygen and hydrogen. The sodium hydroxide is useful elsewhere in the mill and the by-product gases may be vented.

15 The invention is illustrated by the following Example:

An experimental cell was set up as seen in Figure 1. The cell was a conventional MP cell from Electrocell AB which had been modified to accommodate a three-dimensional electrode formed by inserting a graphite felt (Union Carbide Corporation) into the cathode compartment. The cell was divided into anode and cathode compartments by a cation exchange membrane (NAFION 120). The membrane area was 1 sq.dm while the area of the cathode was estimated to be approximately 100 to 1000 times the membrane area. An oxygen-evolving dimensionally-stable electrode was used as the anode.

20 30 Feed to the cathode compartment was 8.626 moles of sodium chlorite, 2.356 moles of sodium chloride and 1.536 moles of HCl. 6N H<sub>2</sub>SO<sub>4</sub> was used as the anolyte. An electrode potential of about -0.7 volts vs. SCE was applied to the cathode at a current density of 1.97 kA/m<sup>2</sup> for a period of 4 hrs at 70 °C. The effluent from the cathode chamber contained 7.659 moles NaClO<sub>3</sub> and 3.548 moles NaCl. The off-gases were analyzed and contained 0.626 moles of ClO<sub>2</sub> and 0.068 moles of Cl<sub>2</sub>.

25 40 The chlorine dioxide had a purity of 90.2%, produced at a chemical efficiency of 82.2%.

45 In summary of this disclosure, the present invention provides a novel electrolyte process for the production of chlorine dioxide in substantially pure form. Modifications are possible within the scope of this invention.

### Claims

1. An electrolytic process for the production of chlorine dioxide, characterized by the steps of
  - (a) providing an electrolytic cell having a cathode compartment with a three-dimensional high surface-area cathode therein and an anode compartment separated from the cathode compartment by a cation-exchange membrane;
  - (b) feeding chlorate ions to the cathode compartment and providing hydrogen ions and chloride ions in the cathode compartment;
  - (c)

reducing the chloride ions with the hydrogen ions and chloride ions in the cathode compartment to form chlorine dioxide while an electric current is applied to the cathode compartment to reduce chlorine co-produced with the chlorine dioxide to chloride ions; (d) venting chlorine dioxide so produced from the cathode compartment; and (e) electrolytically forming hydrogen ions in the anode compartment and transferring the hydrogen ions across an ion exchange membrane from the anode compartment to the cathode compartment.

2. The process claimed in claim 1, characterized in that hydrogen ions and chloride ions in the cathode compartment are provided in part by the hydrogen ions transferred to the cathode compartment from the anode compartment and by the chloride ions produced by electrolytic reduction of the co-produced chlorine, and in part by hydrochloric acid fed to the cathode compartment.

3. The process claimed in claim 1, characterized in that hydrogen ions and chloride ions in the cathode compartment are provided, for hydrogen ions, wholly by the hydrogen ions transferred to the cathode compartment from the anode compartment and, for chloride ions, in part by the chloride ions produced by electrolytic reduction of the co-produced chlorine and in part by chloride ions produced by electrolytic reduction of chlorine fed to the cathode compartment from an external source.

4. The process claimed in claim 3, characterized by integration with a sodium chlorite-producing electrolytic process wherein the vented chlorine dioxide is electrolytically reduced to chlorite ions and chlorine is electrolytically formed and is forwarded to the cathode compartment to provide the chlorine feed thereto, optionally by further integration with a sodium chlorate-producing electrolytic process wherein by-product sodium chloride from the cathode compartment is electrolyzed to provide the sodium chlorate feed to the cathode compartment.

5. The process claimed in claim 3, characterized by integration with a caustic-chlorine cell wherein by-product sodium chloride from the cathode compartment is electrolyzed to provide the chlorine feed to the cathode compartment.

6. The process claimed in any one of claims 1 to 5, characterized in that the catholyte in the cathode compartment has a chloride ion concentration of at least 5 molar, preferably about 5 to about 6.5 molar, preferably in a chlorate-to-chloride ion ratio of about 2:1 to about 4:1, and a total acid normality of at least about 0.01 normal, preferably about 0.05 normal.

7. The process claimed in any one of claims 1 to 6, characterized in that the catholyte in the cathode compartment has a temperature of at least about 50°C, preferably about 60° to about 70°C.

8. The process claimed in any one of claims 1 to 7, characterized in that an electrode potential is applied to the cathode which is more positive than -1 volt as compared with a saturated calomel electrode and as determined at the current feeder to the three-dimensional cathode and more negative than the open circuit potential under the prevailing conditions, preferably about -0.2 volt.

9. The process claimed in any one of claims 1 to 8, characterized in that the cathode comprises stacked layers of electroconductive mesh material through the interstices of which percolates the chlorate solution generally parallel to the current flow, or comprises a packed bed of individual electroconductive particles through which percolates the chlorate solution generally perpendicular to the current flow.

10. The process claimed in claim 9, characterized in that the cathode is constructed of a material having a high overpotential for the reaction  $\text{Cl}_2 \rightarrow \text{Cl}^-$ .

11. The process claimed in claim 10, characterized in that the material having a high overpotential is a carbonaceous material.

12. The process claimed in claim 11, characterized in that the carbonaceous material is graphite.

13. The process of any one of claims 1 to 12, characterized in that the chlorate ions are fed to the cathode compartment in an aqueous solution of sodium chlorate having a concentration of about 3 to about 7 molar.

## Patentansprüche

1. Elektrolytisches Verfahren zur Herstellung von Chlordioxid, gekennzeichnet durch die Schritte (a) Bereitstellen einer Elektrolysezelle mit einem Kathodenabteil, versehen mit einer dreidimensionalen Kathode mit großer Oberfläche

sowie einem Anodenabteil, das von dem Kathodenabteil durch eine Kationenaustauschermembran getrennt ist, (b) Einspeisen von Chlorationen in das Kathodenabteil und Einleiten von Wasserstoffionen und Chloridionen in das Kathodenabteil, (c) Reduzieren der Chlorationen mit den Wasserstoffionen und Chloridionen im Kathodenabteil zur Bildung von Chlor-dioxid, während ein elektrischer Strom an das Kathodenabteil angelegt wird, um das zusammen mit dem Chlordioxid gebildete Chlor zu Chloridionen zu reduzieren, (d) Abblasen des gebildeten Chlordioxid aus dem Kathodenabteil und (e) elektrolytisches Erzeugen von Wasserstoffionen im Anodenabteil und Überleiter der Wasserstoffionen durch eine Ionenaustauschermembran aus dem Anodenabteil zum Kathodenabteil.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß Wasserstoffionen und Chloridionen im Kathodenabteil teilweise durch die Wasserstoffionen dargestellt werden, die aus dem Anodenabteil in das Kathodenabteil überführt werden und durch die Chloridionen, die durch die elektrolytische Reduktion des mitgebildeten Chlors produziert werden, sowie zum Teil durch die Salzsäureeinspeisung in das Kathodenabteil.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß Wasserstoffionen und Chloridionen im Kathodenabteil bezüglich der Wasserstoffionen ganz durch die aus dem Anodenabteil in das Kathodenabteil überführten Wasserstoffionen und bezüglich der Chloridionen teilweise durch die Chloridionen, die durch die elektrolytische Reduktion des mitgebildeten Chlors und teilweise durch Chloridionen, die durch elektrolytische Reduktion der Chloreinspeisung in das Kathodenabteil aus einer externen Quelle produziert werden, geschaffen werden.

4. Verfahren nach Anspruch 3, gekennzeichnet durch die Integration des Verfahrens mit einem elektrolytischen Verfahren zur Herstellung von Natriumchlorit, wobei das abgeblasene Chlordioxid elektrolytisch zu Chloridionen reduziert und Chlor elektrolytisch gebildet wird und in das Kathodenabteil eingeleitet wird, um dort die Chloreinspeisung zu bilden, gegebenenfalls noch durch weitere Integration mit einem elektrolytischen Verfahren zur Herstellung von Natriumchlorat, wobei das als Nebenprodukt im Kathodenabteil gebildete Natriumchlorid elektrolysiert wird zur Bildung der Natriumchlorat-Einspeisung in das Kathodenabteil.

5. Verfahren nach Anspruch 3, gekennzeichnet durch die Integration des Verfahrens mit einem Ätzalkali-Chlor-Elektrolyseverfahren, wobei das Nebenprodukt Natriumchlorid aus dem Kathodenabteil elektrolysiert wird, um die Chloreinspeisung in das Kathodenabteil zu bilden.

6. Verfahren nach den Ansprüchen 1 bis 5, dadurch gekennzeichnet, daß der Katholyt im Kathodenabteil eine Chlorationenkonzentration von wenigstens 5-molar, vorzugsweise etwa 5 bis etwa 6,5-molar hat, vorzugsweise bei einem Verhältnis Chlorationen zu Chloridionen von etwa 2:1 bis etwa 4:1, und einer gesamten Säurenormalität von wenigstens etwa 0,01 n, vorzugsweise etwa 0,05 n.

7. Verfahren nach den Ansprüchen 1 bis 6, dadurch gekennzeichnet, daß der Katholyt im Kathodenabteil eine Temperatur von wenigstens etwa 50 °C, vorzugsweise etwa 60 ° bis etwa 70 °C hat.

8. Verfahren nach den Ansprüchen 1 bis 7, dadurch gekennzeichnet, daß ein Elektrodenpotential an die Kathode gelegt wird, das positiver als -1 Volt ist, verglichen mit einer gesättigten Kalomelelektrode und gemessen an der Stromeinspeisung zur dreidimensionalen Kathode, und daß es negativer als das Potential des offenen Stromkreises ist unter den vorherrschenden Bedingungen, vorzugsweise etwa -0,2 Volt beträgt.

9. Verfahren nach den Ansprüchen 1 bis 8, dadurch gekennzeichnet, daß die Kathode aus aufeinander gelegten Schichten von elektrisch leitfähigem Siebmaterial besteht, durch dessen Zwischenräume die Chloratlösung im allgemeinen parallel zum Stromfluß durchsickert, oder daß sie aus einem gepackten Bett aus einzelnen elektrisch leitfähigen Teilchen besteht, durch welches die Chloratlösung allgemein senkrecht zum Stromfluß durchsickert.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die Kathode aus einem Material aufgebaut ist, das ein hohes Überpotential für die Reaktion  $\text{Cl}_2 \rightarrow \text{Cl}^-$  hat.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das Material mit einem hohen Überpotential ein kohlenstoffhaltiges Material ist.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das kohlenstoffhaltige Material Graphit ist.

13. Verfahren nach den Ansprüchen 1 bis 12, dadurch gekennzeichnet, daß die Chlorationen in das Kathodenabteil als wäßrige Lösung von Natriumchlorat mit einer Konzentration von etwa 3 bis etwa 7- molar eingespeist werden.

5

#### Revendications

1. Procédé d'électrolyse pour produire du dioxyde de chlore, caractérisé en ce qu'il comprend les étapes consistant :

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- (a) à prévoir une cellule électrolytique ayant un compartiment cathodique, lequel contient une cathode tridimensionnelle d'aire élevée, et un compartiment anodique séparé du compartiment cathodique par une membrane échangeuse de cations ;
- (b) à envoyer des ions chlorate dans le compartiment cathodique et à disposer d'ions hydrogène et d'ions chlorure dans le compartiment cathodique ;
- (c) à réduire les ions chlorate à l'aide des ions hydrogène et des ions chlorure dans le compartiment cathodique pour former du dioxyde de chlore par application d'un courant électrique au compartiment cathodique, pour réduire en ions chlorure le chlore produit en même temps que le dioxyde de chlore ;
- (d) à évacuer à l'atmosphère, à partir du compartiment cathodique, le dioxyde de chlore ainsi produit ; et
- (e) à former par voie électrolytique des ions hydrogène dans le compartiment anodique et à transférer les ions hydrogène, en leur faisant traverser la membrane échangeuse d'ions, du compartiment anodique au compartiment cathodique.

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2. Procédé selon la revendication 1, caractérisé en ce que les ions hydrogène et les ions chlorure se trouvant dans le compartiment cathodique sont fournis pour partie par les ions hydrogène transférés du compartiment anodique au compartiment cathodique et par les ions chlorure produits par la réduction électrolytique du chlore produit en même temps, et pour partie par l'acide chlorhydrique introduit dans le compartiment cathodique.

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3. Procédé selon la revendication 1, caractérisé en ce que les ions hydrogène et les ions chlorure se trouvant dans le compartiment cathodique sont, pour ce qui est des ions hydrogène, fournis en totalité par les ions hydrogène transférés au compartiment cathodique à partir du compartiment anodique et, pour ce qui est des ions chlorure, pour partie par les ions

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chlorure produits par la réduction électrolytique du chlore produit en même temps, et pour partie par les ions chlorure produits par la réduction électrolytique du chlore introduit dans le compartiment cathodique à partir d'une source extérieure.

4. Procédé selon la revendication 3, caractérisé par une intégration avec un procédé électrolytique de production de chlorite de sodium, dans lequel le dioxyde de chlore envoyé à l'atmosphère subit une réduction électrolytique en ions chlorite, et le chlore est formé par voie électrolytique et est envoyé au compartiment cathodique pour y fournir la charge de chlore, éventuellement par une intégration plus poussée avec un procédé électrolytique de production de chlorate de sodium dans lequel le sous-produit chlorure de sodium provenant du compartiment cathodique est électrolyisé pour fournir la charge de chlorate de sodium du compartiment cathodique.

5. Procédé selon la revendication 3, caractérisé par une intégration avec une cellule soude-chlore, dans laquelle le sous-produit chlorure de sodium provenant du compartiment cathodique est électrolyisé pour fournir la charge de chlore au compartiment cathodique.

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que la concentration molaire de l'ion chlorate dans le catholyte se trouvant dans le compartiment cathodique est d'au moins 5, de préférence d'environ 5 à environ 6,5, le rapport de l'ion chlorate à l'ion chlorure étant de préférence d'environ 2:1 à environ 4:1, la normalité acide totale étant d'au moins environ 0,01 N, de préférence d'environ 0,05 N.

7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que le catholyte se trouvant dans le compartiment cathodique a une température d'au moins environ 50 °C, de préférence d'environ 60 à environ 70 °C.

8. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce qu'on applique à la cathode un potentiel d'électrode plus positif que -1 V, par rapport à une électrode au calomel saturé, comme déterminé au niveau de la ligne d'alimentation du courant électrique allant vers la cathode tridimensionnelle, et qui est plus négatif que le potentiel en circuit ouvert dans les conditions en vigueur, de préférence d'environ -0,2 V.

9. Procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que la cathode est constituée de couches empilées d'un matériau maillé électroconducteur à travers les interstices duquel s'infiltre par percolation la solution de chlorate généralement d'une manière parallèle à l'écoulement du courant, ou encore comprend un lit garni de particules électroconductrices individuelles à travers lesquelles s'infiltre par percolation la solution de chlorate, d'une manière généralement perpendiculaire à l'écoulement du courant. 5

10. Procédé selon la revendication 9, caractérisé en ce que la cathode est construite en un matériau ayant un excédent de potentiel élevé pour ce qui est de la réaction  $\text{Cl}_2 \rightarrow \text{Cl}^-$ . 10

11. Procédé selon la revendication 10, caractérisé en ce que le matériau ayant un excédent de potentiel élevé est un matériau charbonneux. 15

12. Procédé selon la revendication 11, caractérisé en ce que le matériau charbonneux est le graphite. 20

13. Procédé selon l'une quelconque des revendications 1 à 12, caractérisé en ce que les ions chlorate sont introduits dans le compartiment cathodique dans une solution aqueuse de chlorate de sodium ayant une concentration molaire d'environ 3 à environ 7. 25

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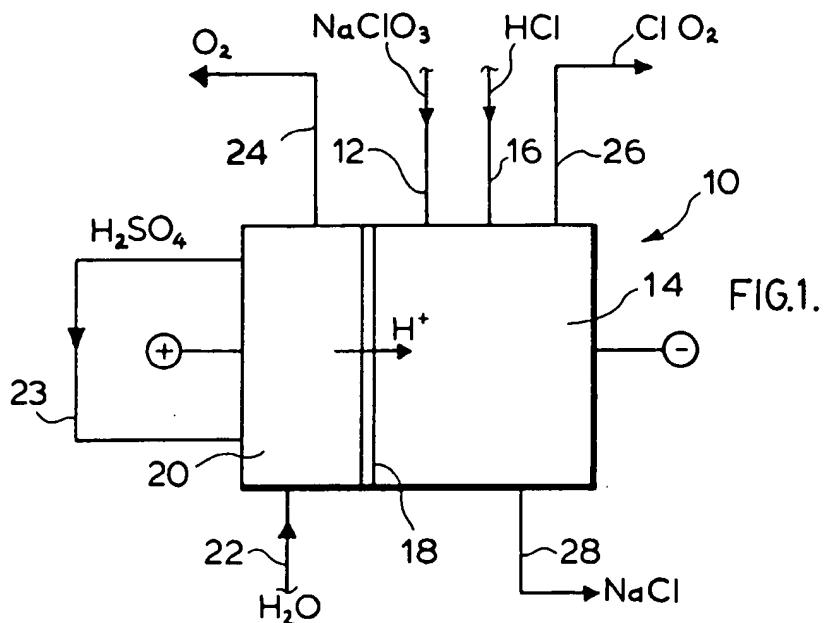


FIG. 3.

